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Spectrophotometric determination of copper(II) after separation by coprecipitation of its 5,7-dichlorooxine complex using naphthalene as an organic coprecipitant

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A spectrophotometric method for the determination of micro amounts of copper(II) after coprecipitation of its 5,7-dichlorooxine complex with naphthalene is described. Copper(II) reacts with 5,7-dichlorooxine to form water-insoluble stable complex. This complex is completely coprecipitated with microfine naphthalene. The co-precipitated mixture of the complex and naphthalene is separated from the aqueous solution by aspiration, dried in a dryer at 60 °C and dissolved in DMF. The absorbance of the solution is measured at 420 nm against a reagent blank and micro amounts of copper(II) are determined spectrophotometrically. Beer's law was obeyed for 5-100 μg of copper(II) in 10 ml of DMF. The molar absorptivity was calculated to be 6.4×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ at 420 nm, and the sensitivity being 0.010 μg of copper(II) per cm^2 for the absorbance of 0.001. The relative standard deviation for the present analysis of copper(II) was 0.84 % for ten determinations.

1 Introduction

5,7-dichlorooxine reacts with various metal ions to form water-insoluble colored complexes. Among these complexes, copper complex is completely coprecipitated with microfine naphthalene in the aqueous solution at pH 4-10.5 by vigorous shaking. After coprecipitation, the mixture of the complex and naphthalene was aspirated through a funnel with a disc shaped teflon filter, washed with water, dried in a dryer and dissolved in DMF. The absorbance of the solution was measured at 420 nm and the micro amounts of copper(II) was determined from a calibration curve. The coprecipitation of the complex with naphthalene was very easily completed by vigorous shaking for several seconds as

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well as naphthalene extraction method. The amount of naphthalene for complete coprecipitation of the complex is very small compared with the naphthalene extraction method. The complex is almost completely coprecipitated and concentrated from the larger volume of aqueous solution with only 0.4 g of naphthalene. In the present paper, the spectrophotometric determination of copper(II) is reported in detail.

2 Experimental method

Reagents and apparatus

Standard copper(II) solution. Prepared by diluting 10 ml of 1000 ppm copper(II) standard solution (Analytical-reagent grade, Wako Pure Chemical Industries LTD, Osaka, Japan) to 1000 ml with water.

Reagent. Use 0.05% 5,7-dichlorooxine solution in ethanol(w/v) and 20% naphthalene solution in acetone(w/v).

The buffer solutions were prepared by mixing 1M acetic acid and 1M ammonium acetate, or 1M ammonia water and 1M ammonium acetate.

All other reagents were reagent-grade and were not purified.

Deionized water was used.

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements with 10 mm glass cell.

The pH measurements were made with a Toa Dempa HM-6A pH meter, equipped with combined glass-calomel electrodes.

Procedure

To about 40 ml of a sample solution containing 1-10 ml of 10 ppm copper solution, in a tightly stoppered Erlenmeyer flask, add 2.0 ml of 0.05% 5,7-dichlorooxine solution and 2.0 ml of the buffer solution (pH 9.0). Mix the solution well, and digest for ten minutes. Add 2.5 ml of 20% naphthalene-acetone solution and shake it vigorously for 1 min. Collect the colored naphthalene mixture on a funnel with disc shaped filter(filter paper, No. 5C). Wash with water and dry in a dryer at about 60 °C. Then dissolve it in DMF and dilute to 10 ml. Measure the absorbance of the solution in 10 mm glass cell against a reagent blank prepared similarly. Calculate the amounts of copper(II) from a calibration curve.

3 Results and discussion

3.1 Absorption spectra

A sample solution containing 50 μg of copper(II), 2.0 ml of 0.05%

5,7-dichlorooxine solution and 2.0 ml of the buffer solution(pH 9.0) was prepared according to the recommended procedure, and the complex formed was coprecipitated with microfine naphthalene by vigorous shaking for 1 min. The coprecipitated mixture was collected on a funnel with disc shaped filter, dried and dissolved in DMF. The absorbances of the solution were measured at various wavelengths between 350 and 450 nm. Fig.1 shows the absorption spectra of the reagent blank and the copper complex in naphthalene-DMF solution. The complex has an absorption maximun at 420 nm, whereas the reagent blank gives small absorption peak between 390 and 430 nm. Therefore, 420 nm was selected as an optimum wavelength for the further study.

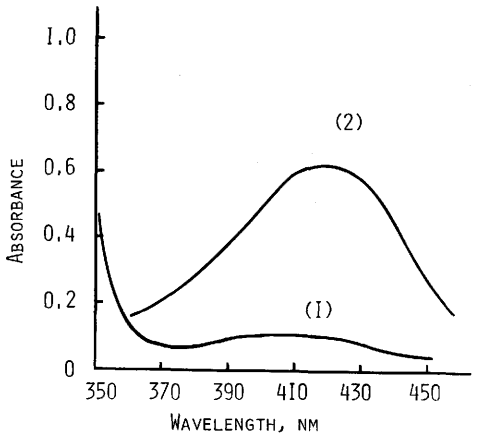

FIG. 1 ABSORPTION SPECTRA OF REAGENT AND COPPER COMPLEX IN NAPHTHALENE-DMF SOLUTION
Cu(II) : 50 μG ; 0.05% 5,7-DICHLORO-OXINE : 2.0 ML ; PH : 9.0 ; DIGESTION TIME : 10 MIN
REFERENCE : (I) AGAINST WATER, (2) AGAINST REAGENT BLANK

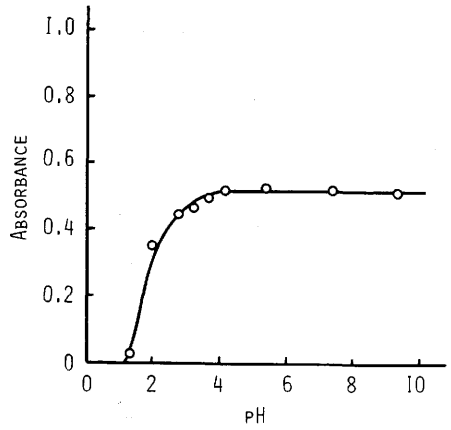

FIG. 2 EFFECT OF PH
Cu : 50 μG ; 0.05% 5,7-DICHLORO-OXINE : 2.0 ML ; NAPHTHALENE-ACETONE : 2.0 ML ; DIGESTION TIME : 10 MIN
REFERENCE : REAGENT BLANK

3.2 Effect of pH

The pH of the sample solution containing 50 μg of copper(II) and 2.0 ml of 0.05% 5,7-dichlorooxine solution was adjusted to 1 -10 with various buffer solution , and the complex was coprecipitated with naphthalene according to the recommended procedure. The pH measurements were made after coprecipitation at room temperature. Fig.2 shows the effect of the pH on the absorbance of the complex in naphthalene-DMF solution. The pH range at which maximal coprecipitation occurs was found to be 4.5 - 10. Therefore, a pH of the solution was adjusted to 9.0 throughout the further study.

3.3 Effect of reagent concentration

The varying amounts of 0.05% 5,7-dichlorooxine solution were added to the sample solution containing 50 μg of copper(II) and 2.0 ml of the buffer solution(pH 9.0), and the coprecipitation was carried out according to the recommended procedure. Fig.3 shows the effect of the reagent concentration on the absorbance of the complex. It can be seen that the absorbance of the complex increased with increasing amounts of the reagent with up to 1.5 ml of this reagent and then remained almost constant. Therefore, 2.0 ml of 0.05% 5,7-dichlorooxine solution were used for the further study.

3.4 Effect of buffer solution

The varying volume of the buffer solution (pH 9.0) was added to the solution containing 50 μg of copper(II) and 2.0 ml of 0.05% 5,7-dichlorooxine solution, and the coprecipitation was carried out according to the recommended procedure.From the experimental result, a range of 0.5-5.0 ml of the buffer solution was practically without effect on the absorbance. Therefore, 2.0 ml of the buffer solution were added for the further study.

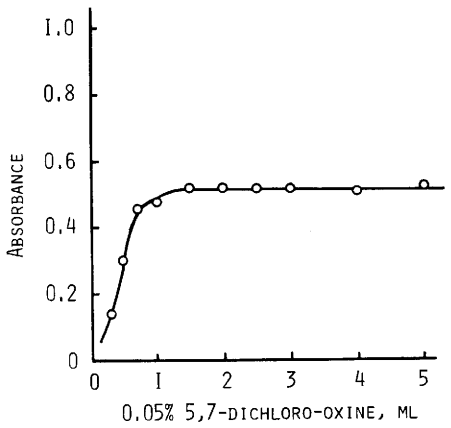

FIG. 3 EFFECT OF REAGENT CONCENTRATION
Cu : 50 μg ; WAVELENGTH : 420 nm ; pH : 9.0 ; 20% NAPHTHALENE-ACETONE : 2.5 ml
REFERENCE : REAGENT BLANK

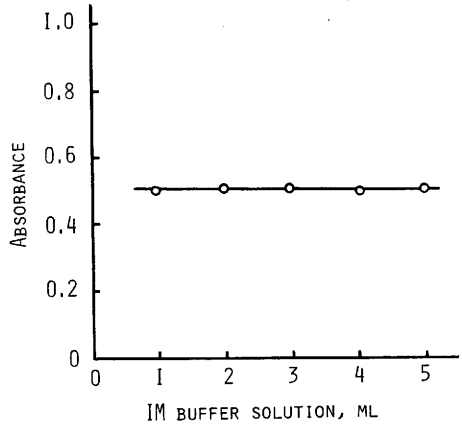

FIG. 4 EFFECT OF ADDITION OF BUFFER SOLUTION
Cu : 50 μg ; WAVELENGTH : 420 nm ; pH : 9.0 ; 0.05% 5,7-DICHLORO-OXINE : 2.0 ml ; DIGESTION TIME 10 min ; SHAKING TIME : 1 min
REFERENCE : REAGENT BLANK

3.5 Effect of digestion time

The complex in the solution was digested at room temperature

and the effect of digestion time on the absorbance was examined. From the experimental result, the absorbance did not change by digestion for 30 min. Therefore, 10 min of digestion time were selected for the further study.

3.6 Effect of naphthalene-acetone solution

Varying amounts of naphthalene-acetone solution was added to the solution containing the copper complex. Fig.5 shows the effect of addition of naphthalene-acetone solution on the absrbance of the complex. The absorbance increased with increasing amounts of naphthalene-acetone solution up to 1.0 ml of 20% solution, and the addition of 1.0 - 5.0 ml did not give the change in the absorbance. Therefore, 2.5 ml of 20% naphthalene-acetone solution were added for the further study.

3.7 Effect of shaking time

The mixture of the copper complex and naphthalene in the solution was vigorously shaked between 3 seconds and 2 minutes. This period of shaking time was demonstrated to be quite sufficient for the complete coprecipitation of the complex.

3.8 Effect of standing time

The mixture of the copper complex and naphthalene was dissolved

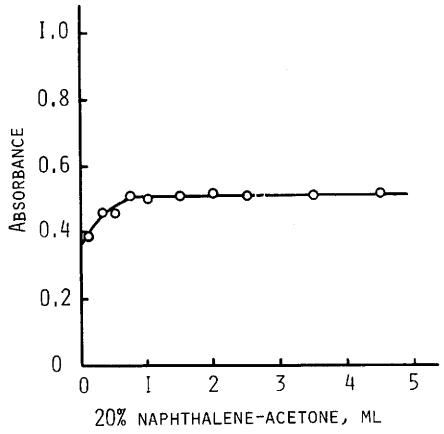

Fig. 5 Effect of addition of naphthalene
Cu : 50 μg ; Wavelength : 420 nm ; pH : 9.0 ;
Buffer solution : 2.0 ml ; Shaking time : 1 min ;
Digestion time : 10 min
Reference : Reagent blank

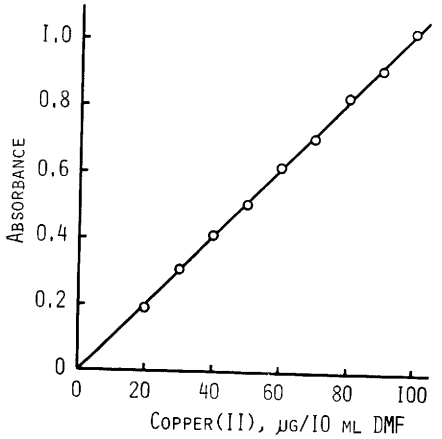

Fig. 6 Calibration curve for copper
Wavelength : 420 nm ; pH : 9.0 ; 0.05% 5,7-dichloro-oxine : 2.0 ml ; Buffer solution : 2.0 ml ; 20% naphthalene-acetone : 2.5 ml ; Shaking time : 1 min ; Standing time : 10 min
Reference : Reagent blank

in DMF and the effect of standing time on the absorbance was examined between 5 minutes and 2 hours. The color of the complex in DMF solution was very stable and this period of standing time did not give the marked change in the absorbance.

3.9 Calibration curve

Under the optimum conditions described above, the calibration curve for the copper determination was constructed. Beer's law was obeyed over the range of 5 - 100 μg of copper(II) in 10 ml of DMF. The molar absorptivity was calculated to be 6.4×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ at 420 nm, the sensitivity being 0.010 $\mu g/cm^2$ for an absorbance of 0.001. Ten sample solutions containing 50 μg of copper(11), prepared by the recommended procedure, gave a mean absorbance of 0.510, with a standard deviation of 0.0043 (relative standard deviation of 0.84%).